

AMENDMENT(S) TO THE CLAIMS

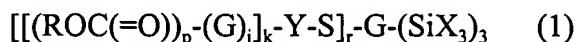
This listing of claims will replace all prior versions and listings of claims in this application:

Listing of Claims:

1. (Currently amended) A method for increasing the hardness of silica/rubber mixtures comprising blending with said mixture at least one silane and a hardness-increasing amount of at least one member selected from the group consisting of thixotropic fumed silica, precipitated silica wherein the total amount of silica is up from 80 phr to 110 phr, an MQ resin wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, and R^a , R^b , and R^c are the same or different functional or non-functional organic groups, a thermoplastic resin selected from the group consisting of high-density polyethylene, ultra high molecular weight polyethylene and low density-polyethylene and a thermosetting resin, wherein the silane is a blocked mercaptosilane, and wherein the silica/rubber mixture optionally includes inorganic filler,

and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of the silica/rubber mixture of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyldisulfide) as the silane, and,

wherein the blocked mercaptosilane has a formula selected from the group consisting of:



and



or is a compound compound selected from the group consisting of 2-triethoxysilyl-1-ethyl thioacetate, 2-trimethoxysilyl-1-ethyl thioacetate, 2-(methyldimethoxysilyl)-1-ethyl thioacetate, 3-trimethoxysilyl-1-propyl thioacetate, triethoxysilylmethyl thioacetate, trimethoxysilylmethyl thioacetate, triisopropoxysilylmethyl thioacetate, methyldiethoxysilylmethyl thioacetate, methyldimethoxysilylmethyl thioacetate, methyldiisopropoxysilylmethyl thioacetate, dimethylethoxysilylmethyl thioacetate, dimethylmethoxysilylmethyl thioacetate, dimethylisopropoxysilylmethyl thioacetate, 2-triisopropoxysilyl-1-ethyl thioacetate, 2-(methyldiethoxysilyl)-1-ethyl thioacetate, 2-(methyldiisopropoxysilyl)-1-ethyl thioacetate, 2-(dimethylethoxysilyl)-1-ethyl thioacetate, 2-(dimethylmethoxysilyl)-1-ethyl thioacetate, 2-(dimethylisopropoxysilyl)-1-ethyl thioacetate, 3-triethoxysilyl-1-propyl thioacetate, 3-triisopropoxysilyl-1-propyl thioacetate, 3-methyldiethoxysilyl-1-propyl thioacetate, 3-methyldimethoxysilyl-1-propyl thioacetate, 3-methyldiisopropoxysilyl-1-propyl thioacetate, 1-(2-triethoxysilyl-1-ethyl)-4-thioacetylhexane, 1-(2-triethoxysilyl-1-ethyl)-3-thioacetylhexane, 2-triethoxysilyl-5-thioacetylnorbornene, 2-triethoxysilyl-4-thioacetylnorbornene, 2-(2-triethoxysilyl-1-ethyl)-5-thioacetylnorbornene, 2-(2-triethoxysilyl-1-ethyl)-4-thioacetylnorbornene, 1-(1-oxo-2-thia-5-triethoxysilylpenyl)benzoic acid, 6-triethoxysilyl-1-hexyl thioacetate, 1-triethoxysilyl-5-hexyl thioacetate, 8-triethoxysilyl-1-octyl thioacetate, 1-triethoxysilyl-7-octyl thioacetate, 6-triethoxysilyl-1-hexyl thioacetate, 1-triethoxysilyl-5-octyl thioacetate, 8-trimethoxysilyl-1-octyl thioacetate, 1-trimethoxysilyl-7-octyl thioacetate, 10-triethoxysilyl-1-decyl thioacetate, 1-triethoxysilyl-9-decyl thioacetate, 1-triethoxysilyl-2-butyl thioacetate, 1-triethoxysilyl-3-butyl thioacetate, 1-triethoxysilyl-3-methyl-2-butyl thioacetate, 1-

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triethoxysilyl-3-methyl- 3-butyl thioacetate, 3-trimethoxysilyl-1-propyl thiooctoate, 3-triethoxysilyl-1-propyl thiopalmitate, 3-triethoxysilyl-1-propyl thiooctoate, 3-triethoxysilyl-1-propyl thiobenzoate, 3-triethoxysilyl-1-propyl thio-2-ethylhexanoate, 3-methyldiacetoxysilyl-1-propyl thioacetate, 3-triacetoxysilyl-1-propyl thioacetate, 2-methyldiacetoxysilyl-1-ethyl thioacetate, 2-triacetoxysilyl-1-ethyl thioacetate, 1-methyldiacetoxysilyl-1-ethyl thioacetate, 1-triacetoxysilyl-1-ethyl thioacetate, bis-(3-triethoxysilyl-1-propyl)ethyl dithiophosphonate, 3-triethoxysilyl-1-propyldimethyl thiophosphinate, 3-triethoxysilyl-1-propyldiethyl thiophosphinate, bis-(3-triethoxysilyl-1-propyl)methyl trithiophosphonate, bis-(3-triethoxysilyl-1-propyl)ethyl trithiophosphonate, 3-triethoxysilyl-1-propyldimethyl dithiophosphinate, 3-triethoxysilyl-1-propyldiethyl dithiophosphinate, bis-(3-methyldimethoxysilyl-1-propyl)methyl dithiophosphonate, bis-(3-methyldimethoxysilyl-1-propyl)ethyl dithiophosphonate, 3-methyldimethoxysilyl-1-propyldiethyl thiophosphinate, 3-methyldimethoxysilyl-1-propylmethanethiosulphonate, 3-triethoxysilyl-1-propylethane thiosulphonate, 3-triethoxysilyl-1-propylbenzene thiosulphonate, 3-triethoxysilyl-1-propyl- toluene thiosulphonate, 3-triethoxysilyl-1-propynaphthalene thiosulphonate, 3-triethoxysilyl-1-propylxylene thiosulphonate, triethoxysilylmethylmethyl thiosulphate, triethoxysilylmethylmethane thiosulphonate, triethoxysilylmethylethane thiosulphonate, triethoxysilylmethylbenzene thiosulphonate, triethoxysilylmethyltoluene thiosulphonate, triethoxysilylmethylnaphthalene thiosulphonate and triethoxysilylmethylxylene thiosulphonate,

wherein

Y is a polyvalent species $(D)_z A' (=E)$, each wherein the atom (A') attached to the unsaturated heteroatom (E) is attached to the sulfur, which in turn is linked via a group G to the silicon atom;

each R is chosen independently from hydrogen, straight, cyclic, or branched alkyl that may or may not contain unsaturation, alkenyl groups, aryl groups, and aralkyl groups wherein each R contains from 1 to 18 carbon atoms;

each G is independently a monovalent or polyvalent group derived by substitution of alkyl, alkenyl, aryl, or aralkyl wherein G can contain from 1 to 18 carbon atoms, with the proviso that G is not such that the silane would contain an α,β -unsaturated carbonyl including a carbon-carbon double bond next to the thiocarbonyl group, and if G is monovalent wherein p = 0, G can be a hydrogen atom;

X is independently a group selected from the group consisting of -Cl, -Br, RO-, $RC(=O)O-$, $R_2C=NO-$, R_2NO- or R_2N- , -R, $-(OSiR_2)_1(OSiR_3)$ wherein each R is as above and at least one X is not -R;

D is oxygen, sulfur, or (-NR-);

A' is carbon, sulfur, phosphorus, or sulfonyl;

E is oxygen, sulfur, or NR;

p is 0 to 5; r is 1 to 3; z is 0 to 2; q is 0 to 6; a is 0 to 7; b is 1 to 3; j is 0 to 1, but it may be 0 only if p is 1; c is 1 to 6; t is 0 to 5; s is 1 to 3; k is 1 to 2, with the provisos that

(A) if A' is carbon, sulfur, or sulfonyl, then

(i) $a + b = 2$ and

(ii) $k = 1$;

(B) if A' is phosphorus, then $a + b = 3$ unless both (i) $c > 1$ and (ii) $b = 1$, in which case $a = c + 1$; and

(C) if A' is phosphorus, then k is 2 .

2. (Cancelled)

3. (Cancelled)

4. (Previously presented) The method of claim 1 wherein the rubber is selected from the group consisting of solution styrene-butadiene rubber, emulsion styrene-butadiene rubber, natural rubber, polybutadiene, ethylene-propylene co- and terpolymers, acrylonitrile-butadiene rubber, isoprene, polystyrene and poly α -methyl styrene, cis-1,4-polyisoprene rubber, styrene/butadiene copolymer rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis-1,4-polybutadiene, vinyl polybutadiene rubber, styrene/isoprene copolymers, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubbers containing 2 to 40 weight percent bound acrylonitrile in the terpolymer and combinations thereof .

Claim 5, (Cancelled).

6. (Original) The method of claim 1 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

7. (Original) The method of claim 1 wherein the silica/rubber mixture further comprises an inorganic filler.

8. (Previously presented) The method of claim 7 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc and wollastonite.

9. (Previously presented) The method of claim 1 wherein the at least one member is thixotropic-(hydrophilic and hydrophobic) fumed (pyrogenic) silica.

Claims 10 to 13, (Cancelled).

14. (Original) The method of claim 9 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

15. (Original) The method of claim 9 wherein the silica/rubber mixture further comprises an inorganic filler.

16. (Previously presented) The method of claim 15 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc and wollastonite.

17. (Original) The method of claim 1 wherein the member is precipitated silica.

Claims 18 to 21, (Cancelled).

22. (Original) The method of claim 17 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

23. (Original) The method of claim 17 wherein the silica/rubber mixture further comprises an inorganic filler.

24. (Previously presented) The method of claim 23 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc and wollastonite.

25. (Currently amended) A method for increasing the hardness of silica/rubber mixtures comprising blending with said mixture at least one silane and a hardness-increasing amount of an MQ resin wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, and R^a , R^b , and R^c are the same or different

functional or non-functional organic groups, wherein the silane is a blocked mercaptosilane, and wherein the silica/rubber mixture optionally includes inorganic filler,

and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of the silica/rubber mixture of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyldisulfide) as the silane.

Claims 26 to 29, (Cancelled).

30. (Original) The method of claim 25 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

31. (Original) The method of claim 25 wherein the silica/rubber mixture further comprises an inorganic filler.

32. (Previously presented) The method of claim 31 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc and wollastonite.

33. (Currently amended) The method of claim 1 ~~wherein the at least one member further includes including the step of blending carbon black into the mixture.~~

34. (Original) The method of claim 33 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

35. (Previously presented) The method of claim 1 wherein the at least one member is the thermoplastic resin.

36. (Previously presented) The method of claim 1 wherein the total amount of silica is above 100 phr.

37. (Original) The method of claim 35 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

38. (Previously presented) The method of claim 1 wherein the at least one member is a thermosetting resin.

Claims 39 to 41 (Canceled)

42. (Currently amended) An article of manufacture comprising a silica/rubber mixture hardened by blending with said mixture at least one silane and a hardness-increasing amount of at least one member selected from the group consisting of thixotropic fumed silica, or precipitated silica wherein the total amount of silica is up from 80 phr to 110 phr, an MQ resin

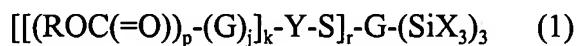
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wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, and R^a , R^b , and R^c are the same or different functional or non-functional organic groups, a thermoplastic resin selected from the group consisting of high-density polyethylene, ultra high molecular weight polyethylene, and low density-polyethylene and a thermosetting resin, wherein the silane is a blocked mercaptosilane, and wherein the silica/rubber mixture optionally includes inorganic filler,

and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of the silica/rubber mixture of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyl disulfide) as the silane, and,

wherein the blocked mercaptosilane has a formula selected from the group consisting of:



and



or is a compound compound selected from the group consisting of 2-triethoxysilyl-1-ethyl thioacetate, 2-trimethoxysilyl-1-ethyl thioacetate, 2-(methyldimethoxysilyl)-1-ethyl thioacetate, 3-trimethoxysilyl-1-propyl thioacetate, triethoxysilylmethyl thioacetate, trimethoxysilylmethyl thioacetate, triisopropoxysilylmethyl thioacetate, methyldiethoxysilylmethyl thioacetate, methyldimethoxysilylmethyl thioacetate, methyldiisopropoxysilylmethyl thioacetate, dimethylethoxysilylmethyl thioacetate, dimethylmethoxysilylmethyl thioacetate, dimethylisopropoxysilylmethyl thioacetate, 2-triisopropoxysilyl-1-ethyl thioacetate, 2-(methyldiethoxysilyl)-1-ethyl thioacetate, 2-(methyldiisopropoxysilyl)-1-ethyl thioacetate, 2-

(dimethylethoxysilyl)-1-ethyl thioacetate, 2-(dimethylmethoxysilyl)-1-ethyl thioacetate, 2-(dimethylisopropoxysilyl)-1-ethyl thioacetate, 3-triethoxysilyl-1-propyl thioacetate, 3-triisopropoxysilyl-1-propyl thioacetate, 3-methyldiethoxysilyl-1-propyl thioacetate, 3-methyldimethoxysilyl-1-propyl thioacetate, 3-methyldiisopropoxysilyl-1-propyl thioacetate, 1-(2-triethoxysilyl-1-ethyl)-4-thioacetylhexane, 1-(2-triethoxysilyl-1-ethyl)-3-thioacetylhexane, 2-triethoxysilyl-5-thioacetylnorbornene, 2-triethoxysilyl-4-thioacetylnorbornene, 2-(2-triethoxysilyl-1-ethyl)-5-thioacetylnorbornene, 2-(2-triethoxysilyl-1-ethyl)-4-thioacetylnorbornene, 1-(1-oxo-2-thia-5-triethoxysilylpenyl)benzoic acid, 6-triethoxysilyl-1-hexyl thioacetate, 1-triethoxysilyl-5-hexyl thioacetate, 8-triethoxysilyl-1-octyl thioacetate, 1-triethoxysilyl-7-octyl thioacetate, 6-triethoxysilyl-1-hexyl thioacetate, 1-triethoxysilyl-5-octyl thioacetate, 8-trimethoxysilyl-1-octyl thioacetate, 1-trimethoxysilyl-7-octyl thioacetate, 10-triethoxysilyl-1-decyl thioacetate, 1-triethoxysilyl-9-decyl thioacetate, 1-triethoxysilyl-2-butyl thioacetate, 1-triethoxysilyl-3-butyl thioacetate, 1-triethoxysilyl-3-methyl-2-butyl thioacetate, 1-triethoxysilyl-3-methyl-3-butyl thioacetate, 3-trimethoxysilyl-1-propyl thiooctoate, 3-triethoxysilyl-1-propyl thiopalmitate, 3-triethoxysilyl-1-propyl thiooctoate, 3-triethoxysilyl-1-propyl thiobenzoate, 3-triethoxysilyl-1-propyl thio-2-ethylhexanoate, 3-methyldiacetoxysilyl-1-propyl thioacetate, 3-triacetoxysilyl-1-propyl thioacetate, 2-methyldiacetoxysilyl-1-ethyl thioacetate, 2-triacetoxysilyl-1-ethyl thioacetate, 1-methyldiacetoxysilyl-1-ethyl thioacetate, 1-triacetoxysilyl-1-ethyl thioacetate, bis-(3-triethoxysilyl-1-propyl)ethyl dithiophosphonate, 3-triethoxysilyl-1-propyl dimethyl thiophosphinate, 3-triethoxysilyl-1-propyl diethyl thiophosphinate, bis-(3-triethoxysilyl-1-propyl)methyl trithiophosphonate, bis-(3-triethoxysilyl-

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1-propyl)ethyl trithiophosphonate, 3-triethoxysilyl-1-propyldimethyl dithiophosphinate, 3-triethoxysilyl-1-propyldiethyl dithiophosphinate, bis-(3-methyldimethoxysilyl-1-propyl)methyl dithiophosphonate, bis-(3-methyldimethoxysilyl-1-propyl)ethyl dithiophosphonate, 3-methyldimethoxysilyl-1-propyldiethyl thiophosphinate, 3-methyldimethoxysilyl-1-propylmethanethiosulphonate, 3-triethoxysilyl-1-propylethane thiosulphonate, 3-triethoxysilyl-1-propylbenzene thiosulphonate, 3-triethoxysilyl-1-propyl-toluene thiosulphonate, 3-triethoxysilyl-1-propynaphthalene thiosulphonate, 3-triethoxysilyl-1-propylxylene thiosulphonate, triethoxysilylmethylmethyl thiosulphate, triethoxysilylmethylmethane thiosulphonate, triethoxysilylmethylethane thiosulphonate, triethoxysilylmethylbenzene thiosulphonate, triethoxysilylmethyltoluene thiosulphonate, triethoxysilylmethylnaphthalene thiosulphonate and triethoxysilylmethylxylene thiosulphonate,

wherein

Y is a polyvalent species $(D)_z A' (=E)$, each wherein the atom (A') attached to the unsaturated heteroatom (E) is attached to the sulfur, which in turn is linked via a group G to the silicon atom;

each R is chosen independently from hydrogen, straight, cyclic, or branched alkyl that may or may not contain unsaturation, alkenyl groups, aryl groups, and aralkyl groups wherein each R contains from 1 to 18 carbon atoms;

each G is independently a monovalent or polyvalent group derived by substitution of alkyl, alkenyl, aryl, or aralkyl wherein G can contain from 1 to 18 carbon atoms, with the proviso

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that G is not such that the silane would contain an α,β -unsaturated carbonyl including a carbon-carbon double bond next to the thiocarbonyl group, and if G is monovalent wherein p = 0, G can be a hydrogen atom;

X is independently a group selected from the group consisting of -Cl, -Br, RO-, RC(=O)O-, R₂C=NO-, R₂NO- or R₂N-, -R, -(OSiR₂)₁(OSiR₃) wherein each R is as above and at least one X is not -R;

D is oxygen, sulfur, or (-NR-);

A' is carbon, sulfur, phosphorus, or sulfonyl;

E is oxygen, sulfur, or NR;

p is 0 to 5; r is 1 to 3; z is 0 to 2; q is 0 to 6; a is 0 to 7; b is 1 to 3; j is 0 to 1, but it may be 0 only if p is 1; c is 1 to 6; t is 0 to 5; s is 1 to 3; k is 1 to 2, with the provisos that

(A) if A' is carbon, sulfur, or sulfonyl, then

(i) a + b = 2 and

(ii) k = 1;

(B) if A' is phosphorus, then a + b = 3 unless both (i) c > 1 and (ii) b = 1, in which case a = c + 1; and

(C) if A' is phosphorus, then k is 2 .

43. (Original) The article of claim 42 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

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44. (Currently amended) An article of manufacture comprising a silica/rubber mixture hardened by blending with said mixture at least one silane and a hardness-increasing amount of an MQ resin wherein Q is $\text{SiO}_{4/2}$, M is $\text{R}^a\text{R}^b\text{R}^c\text{SiO}_{1/2}$, and R^a , R^b , and R^c are the same or different functional or non-functional organic groups, wherein the silane is 3-octanoylthio-1-propyltriethoxysilane, and wherein the silica/rubber mixture optionally includes inorganic filler, and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of the silica/rubber mixture of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyldisulfide) as the silane.

45. (Previously presented) The article of claim 44 wherein said article is a tread portion of a tire.

46. (Previously presented) The article of claim 42 wherein the total amount of silica is above 100 phr.

47. (New) A method for increasing the hardness of silica/rubber mixtures comprising blending with said mixture at least one silane coupling agent and a hardness-increasing amount of silica wherein the total amount of silica is from 80 phr to 110 phr, wherein the silane coupling agent is 3-octanoylthio-1-propyltriethoxysilane,

and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyldisulfide) as the silane.

48. (New) An article of manufacture comprising a silica/rubber mixture hardened by blending with said mixture at least one silane coupling agent and a hardness-increasing amount of silica wherein the total amount of silica is from 80 phr to 1.10 phr, wherein the silane coupling agent is 3-octanoylthio-1-propyltriethoxsilane, and wherein the silica/rubber mixture optionally includes inorganic filler,

and wherein said hardness increasing amount is sufficient to achieve a Shore A hardness of from 56 to 63 and which is above the amount necessary to achieve equivalent Shore A hardness of the silica/rubber mixture as compared with the use of an equivalent molar amount of bis-(triethoxysilylpropyldisulfide) as the silane.

49. (New) The method of claim 25 wherein the silica/rubber mixture comprises a rubber selected from the group consisting of solution styrene-butadiene rubber (SSBR), styrene-butadiene rubber (SBR), natural rubber (NR), polybutadiene (BR), ethylene-propylene co- and terpolymers (EP, EPDM), and acrylonitrile-butadiene rubber (NBR), isoprene rubber, 1,3-butadiene, styrene and methyl styrene, natural or synthetic cis-1,4-polyisoprene rubber, emulsion polymerization prepared styrene/butadiene copolymer rubber, organic solution polymerization

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prepared styrene/butadiene rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, cis-1,4-polybutadiene, vinyl polybutadiene rubber styrene/isoprene copolymers, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber.